These orbitals are of tetragonal antiprism symmetry D_{4d}. The Z axis coincides with the fourfold axis.

A function orthogonal to $\psi_1, \cdots \psi_8$ is given by

$$\psi_9 = (\sin\alpha)s + (\cos\alpha)d_z. \quad (19)$$

The functions were used in constructing Tables I and II. In Table I, S and θ_1 were obtained with $0 \leq \alpha \leq \pi/2$. In Table II, S and θ_1 were obtained with $0 \geqslant \alpha \geqslant -\pi/2$. Here S is the maximum value of ψ_1 and is called the strength of an orbital; θ_1 is the angle between the axis and the maximum in ψ_1 and is approximately the angle between the axis and bond one.

It is evident that the orbitals described in Table I will be preferred since they are stronger than the corresponding ones in Table II. The strongest tetragonal antiprism orbitals may be formed when n equals 0.9047. The maximum strength, 2.988, is only slightly less than the maximum strength[6] of an spd orbital. When the s and d orbitals are of almost equal stability, n will tend to equal 0.9047 if the tetragonal antiprism structure is assumed.

Kimball[1] reasoned that the stable bond arrangement when n equaled one was the dodecahedral arrangement since $[Mo(CN)_8]^{-4}$ has this structure. However, one would conclude from the present calculations that the tetragonal antiprism structure is one of the stable structures when n equals one.

Because of the repulsion between the attached groups in the tetragonal antiprism structure, the acute angle between the axis and a bond will tend to be different from θ_1 for all but one value of n and the effective strength of the orbitals will be reduced somewhat. If the repulsion tends to stabilize the regular tetragonal antiprism structure, this acute angle would tend to be between θ_1 and 59° 16′. (Here a regular tetragonal antiprism is defined as the square antiprism with sixteen equal edges.)

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Compressibilities, Force Constants, and Interatomic Distances of the Elements in the Solid State

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Available data for the compressibilities of crystalline elements are used to calculate the force constants for the assumed Hooke's law interactions between adjacent atoms. On comparison of these constants and the equilibrium interatomic distances it is found that for many substances there holds the relation discovered by Badger for diatomic gas molecules: a linear relation between the reciprocal of the cube root of the force constant and the interatomic distance, for elements of a given row in the periodic table. Deviations from this relation are in the direction of increased compressibility. They are explained as resulting from changes in bond type (that is, in electronic structure) that permit the crystal to adjust itself to the increased pressure.

INTRODUCTION

THE compressibilities of elements and compounds in the solid state[1] represent a considerable body of information which may be interpreted in terms of molecular constants. An attempt is made here to do this for substances which have simple structures, mainly those with cubic symmetry. Our considerations have been based on the concept of the existence of covalent bonds between nearest neighbors in the lattice (resonating covalent bonds in the metals). The compressibility is then used to evaluate the force constant for a Hooke's law force acting along the bonds. A relationship similar to Badger's rule[2] for molecules in the gaseous state has been found to obtain between these force constants and the interatomic distances.

There exists one difficulty with the attempt to use central forces to explain the elastic properties of crystalline matter, especially in the case of metals. Central forces imply certain relations among the various elastic constants of a crystal, the Cauchy relations, which are poorly satisfied for metals.[3] Non-central forces should, therefore, be introduced in addition to the central forces assumed above. In the usual electron theory of metals the interactions between the free electrons and the lattice of residual ion cores are of the non-central type, and the breaking down of the Cauchy relations may be thus accounted for. If all elastic constants are known for a given crystal the contributions to the energy of the crystal from the free electrons may be separated

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† Contribution No. 1380.

[1] See P. W. Bridgman, Rev. Mod. Phys. **18**, 1 (1946).

[2] R. M. Badger, J. Chem. Phys. **2**, 128 (1934); **3**, 710 (1935).

[3] It was recently pointed out by P. S. Epstein (Phys. Rev. **70**, 915 (1946)) that the Cauchy relations are not expected to hold for the general case of central forces involving non-nearest neighbors also. However, they should be satisfied for central forces between nearest neighbors only. Cf. also C. Zener, Phys. Rev. **71**, 323 (1947).

TABLE I. Compressibilities and derived properties of the elements and some compounds.

Substance	Crystal structure[a]	D_0, A[b]	$A \times 10^7$ cm²/kg	$B \times 10^{12}$ cm⁴/kg²	$k \times 10^3$ [c]	$k^{-\frac{1}{4}}$	$-k' \times 10^{-5}$ [d]	Ref.[m]
Ag	*A*1	2.883	9.87	5.06	30.4	3.20	133	B 7
Al	*A*1	2.858	13.43	6.2	22.14	3.561	57	B 7
Au	*A*1	2.878	5.77	3.4	51.9	2.68	500	B 7
B			5.51	2.2				B 3
Ba	*A*2	4.343	101.9	129	7.241	5.168	1.20	B 1
Be	*A*3	2.224[e]	2.20[h]	0.70[h]	33.6[e]	3.10[e]	233[i]	B 6
		2.268[f]	2.82[i]	1.67[i]	26.5[f]	3.36[f]		
C(diam)	*A*4	1.542	1.73		609	1.18		W
Ca	*A*1	3.932	56.97	63.9	7.179	5.184	5.30	B 7
Cb	*A*2	2.853	5.700	2.22	85.0	2.27	523	B 6
Cd	*A*3	3.287[e]	18.3[h]		6.43[e]	5.38[e]		B 1
		2.973	2.1[i]		61.4[f]	2.54[f]		
Ce	*A*3	3.64	45.63	−161.4	8.29	4.94	−59.8	B 1
Co	*A*3	2.503	5.39	2.3	48.4	2.74	400	B 7
Cr	*A*2	2.493	5.19	2.19	81.6	2.31	701	B 1
Cs	*A*2	5.24	700	10,000[k]	1.27	9.22	0.7	L
Cu	*A*1	2.551	7.19	3.0	36.9	3.00	210	B 7
Fe	*A*2	2.478	5.826	0.80	72.26	2.401	118	B 9
Ga	*A*11		20					B 1
Ge	*A*4	2.445	14.11	6.09	117.7	2.040	297	B 7
Hf	*A*3	3.170	9.01	2.37	36.6	3.01	66.5	B 1
In	*A*6	3.242	25					B 1
		3.370						
Ir	*A*1	2.709	2.68	1.3	105	2.12	200	B 1
K	*A*2	4.618	356.5	285	2.201	7.686	1.78	L
La	*A*3	3.741	35.13	14.7	11.10	4.482	1.73	B 1
Li	*A*2	3.04	86.92	97.5	5.94	5.52	1.70	B 1
Mg	*A*3	3.189[e]	9.84[h]	6.51[h]	11.4[e]	4.45[e]	23.1[d]	B 1
		3.202[f]	9.84[i]	9.19[i]	11.2[f]	4.47[f]		
Mn	*A*6, *A*12, *A*13		7.91[l]	5.3				B 3
Mo	*A*2	2.720	3.60	1.19	128	1.98	1150	B 7
Na	*A*2	3.72	156.2	300	4.05	6.27	0.75	L
Nd	*A*3	3.639	32.6		11.6	4.42		B 10
Ni	*A*1	2.487	5.29	2.4	48.9	2.73	450	B 7
Pb	*A*1	3.492	23.72	20.3	15.31	4.027	34.4	B 7
Pd	*A*1	2.745	5.28	2.4	54.1	2.64	450	B 7
Pr	*A*3	3.648	33.8	13	11.2	4.47	1.3	B 1
Pt	*A*1	2.769	3.60	1.8	80.0	2.32	1100	B 7
Rb	*A*2	4.87	520	5600[k]	1.59	8.57	1.1	L
Rh	*A*1	2.684	3.606	2.73	77.43	2.345	1730	B 6
Ru	*A*3	2.672	3.42	2.13	81.3	2.31	1570	B 6
Si	*A*4	2.346	11.2		142	1.91		B 10
Sn, white	*A*5	3.17[g]	6.719[h]	4.07[h]	33.13[g]	3.113[g]		B 1
		3.016[e]	6.022[i]	4.20[i]	51.30[e]	2.691[e]		
Sn, grey	*A*4	2.80	19		100	2.16		T
Sr	*A*1	4.296	81.22	100.6	5.502	5.662	2.02	B 7
Ta	*A*2	2.854	4.79	0.4	101	2.15	79	B 7
Ti	*A*3	2.934	7.97	−0.12	38.3	2.97	46	B 1
Tl	*A*3	3.427	27.8		12.8	4.27		RW, B 1
U	*A*2, *A*15		9.66[l]	3.26				B 7
V	*A*2	2.627	6.09	2.58	73.3	2.39	498	B 1
W	*A*2	2.735	3.18	1.4	146	1.90	2060	B 1
Zn	*A*3	2.907[e]	13.50[h]	7.68[h]	7.975[e]	5.005[e]		B 8
		2.659[f]	1.59[i]	0.78[i]	71.78[f]	2.406[f]		
Zr	*A*3	3.195	10.97	7.44	30.30	3.207	148	B 1
AgBr	*B*1	2.77	27		30	3.2		RB
AgCd	*B*2	2.88	11.54	4.6	42.4	2.87		B 7
AgCl	*B*1	2.46	24		30	3.2		RJ
AgI	*B*3	2.80	40		48	2.8		RJ
AgZn	*B*2	2.74	10.30	1.9	45.0	2.81		B 7
AlSb	*B*3	2.685	18.02	19.0	99.6	2.16		B 4
AuZn	*B*2	2.73	7.54	2.4	61.4	2.54		B 7
BaS	*B*1	3.19	28.93	52.1	32.4	3.14		B 5
CaS	*B*1	2.84	22.80	38.8	36.7	3.01		B 5
CdTe	*B*3	2.80	23.3	12.2	81.6	2.31		B 4
CsI	*B*2	3.95	84.03	201.9	7.98	5.01		B 5
CuBr	*B*3	2.46	28.7	25.1	58.2	2.58		B 5
CuCl	*B*3	2.34	24.63	14.1	64.7	2.49		B 5
CuI	*B*3	2.62	27.52		64.6	2.49		B 5
CuZn	*B*2	2.55	8.95	2.5	48.4	2.74		B 7
HgTe	*B*3	2.79	19.8	25	95.7	2.19		B 4
KI	*B*1	3.53	83.7	150.7	12.4	4.32		B 1

TABLE I.—*Continued.*

Substance	Crystal structure[a]	D_0, A[b]	$A\times10^7$ cm²/kg	$B\times10^{12}$ cm⁴/kg²	$k\times10^{3}$ [c]	$k^{-\frac{1}{3}}$	$-k'\times10^{-5}$ [d]	Ref.[m]
LiI	*B*1	3.00	58.89	107.4	15.0	4.06		B 5
Mg_2Pb	*C*1	2.96	26.13	21.2	38.5	2.96		B 7
NaI	*B*1	3.23	69.36		13.7	4.18		B 5
PbS	*B*1	2.97	18.4	6.33	47.5	2.76		B 2
PbSe	*B*1	3.07	20.67	12.8	43.7	2.84		B 7
PbTe	*B*1	3.22	25.55	24.3	37.1	3.00		B 7
RbI	*B*1	3.66	93.8	197.7	11.5	4.43		B 1
SrS	*B*1	3.01	23.83	38.6	37.1	3.00		B 5
TiC	*B*1	2.16	4.72	2.2	135	1.95		B 1
TiN	*B*1	2.20	3.32	2.13	195	1.72		B 1
TlBr	*B*2	3.44	52		11.2	4.5		RJ
TlCl	*B*2	3.33	48		11.8	4.4		RJ
TlI	*B*2	3.62	68		9.0	4.8		RJ
ZnS (sphalerite)	*B*3	2.35	12.81		124.5	2.00		B 2
ZnS (wurtzite)	*B*4	2.36	13.1		122	2.01		M
ZnO	*B*4	2.01	7.5		182	1.8		M

[a] M. C. Neuburger, Zeits. f. Krist. **93**, 1 (1936), or "Strukturbericht."
[b] In case of alternate structures the one most commonly occurring indicated in table was used for calculations.
[c] k in megadynes/cm.
[d] k' in megadynes/cm².
[e] For bonds inclined to axis of highest symmetry.
[f] For bonds perpendicular to axis of highest symmetry.
[g] For bonds parallel to axis of highest symmetry.
[h] Linear compression parallel to axis of highest symmetry.
[i] Linear compression perpendicular to axis of highest symmetry.
[j] Average value calculated from volume compressibility.
[k] Estimated value.
[l] Crystalline modification investigated not reported.
[m] References to Table I:
B 1 to B 10, P. W. Bridgman:
B 1, *The Physics of High Pressure* (London, 1931).
B 2, Am. J. Sci. **10**, 483 (1925).
B 3, Proc. Am. Acad. **64**, 51 (1929).
B 4, *Ibid.* **66**, 255 (1931).
B 5, *Ibid.* **67**, 345 (1932).
B 6, *Ibid.* **68**, 27 (1933).
B 7, *Ibid.* **70**, 285 (1935).
B 8, Phys. Rev. **47**, 393 (1935).
B 9, Rev. Modern Phys. **18**, 1 (1946).
B 10, Extrapolated from compressibilities to 100,000 kg/cm², (private communication); see Proc. Am. Acad. **76**, 55 (1948).
L, Landolt and Börnstein.
M, F. Madelung and R. Fuchs, Ann. d. Physik **65**, 289 (1921).
RB, T. W. Richards and E. P. Bartlett, J. Am. Chem. Soc. **37**, 470 (1915).
RJ, T. W. Richards and G. Jones, *ibid.* **31**, 158 (1909).
RW, T. W. Richards and J. D. White, *ibid.* **50**, 3290 (1928).
T, G. Tammann and R. Kohlhass, Zeits. f. anorg. u. allgem. Chemie **199**, 209 (1931); estimated from graph on p. 223.
W, E. D. Williamson, J. Franklin Inst. **193**, 491 (1922); S. Bhagavantam and J. Bhimasenachar, Proc. Roy. Soc. (London) **A187**, 381 (1946).

from the interactions between the ion cores, and force constants for the latter may be evaluated,[4] which, however, do not contain the large part of the contribution of the free electrons which can be approximated by central forces. From our viewpoint of nearest-neighbor bonds, where the bulk of the interatomic interactions is described by a central force field, the breakdown of the Cauchy relations may be understood by assuming the operation of forces which oppose deformations of bond angles; these forces are non-central in character. For some crystals with cubic face-centered and cubic body-centered structures these angular force constants were calculated by us from the elastic constants available, and were found to be small compared to the bond stretching constants. They were negative in sign, indicating decrease of the angular potential energy upon angular deformation, and thus implying the existence of a small angular strain for the cases investigated. Unfortunately not enough data on elastic constants are available to permit the systematization of these angular force constants.

METHOD AND RESULTS

If there are n equivalent nearest-neighbor bonds of length D_0 in the unit cell of volume V_0 of a cubic crystal, then the force constant k in the equation $U(D)=(k/2)(D-D_0)^2$ for the potential energy of a bond under compression is given by the expression

$$k=\frac{9V_0}{nD_0^2A}, \tag{1}$$

where A is defined by the equation

$$(V_0-V)/V_0=Ap-Bp^2 \tag{2}$$

relating the volume at pressure p to the volume at zero pressure. Equation (1) applies also to the case of hexagonal closest packing, and was assumed to hold in addition for approximate hexagonal closest packing, as exemplified by a number of metals crystallizing with the $A3$ structure.[5] If A is measured in 10^{-7} cm²/kg, D_0 in A, and k in megadynes/cm Eq. (1) reduces to

$$k=C(D_0/A),$$

where C equals 0.1040 for the lattices $A1$ and $A3$, 0.1699 for the lattice $A2$, and 0.6794 for the lattice $A4$.

From the constant B in Eq. (2) the variation of the force constant k with distance can be calculated. If the expansion

$$k(D)=k+(D-D_0)k' \tag{3}$$

is used we obtain

$$k'=\frac{3(A^2-B)}{A^2D_0}k. \tag{4}$$

[4] K. Fuchs, Proc. Roy. Soc. (London) **153A**, 622 (1936); **157A**, 444 (1936); P. C. Fine, Phys. Rev. **56**, 355 (1939); R. B. Leighton, Thesis, California Institute of Technology, 1947; etc.

[5] The symbols $A3$, etc., are those used in the Strukturbericht.

It was assumed that this equation remains valid for approximate hexagonal closest packing.

For the metals beryllium, magnesium, zinc, and cadmium, with the $A3$ structure, and for the tetragonal modification of tin, the linear compressibilities under hydrostatic pressure parallel and perpendicular to the axis of highest symmetry are known. From these data force constants for the two types of nearest-neighbor bonds in the crystals considered were calculated from simple elastostatic considerations neglecting bond-angle restoring forces. For the $A3$ structure the following results were obtained:

$$k_1=\frac{3c^2-2a^2}{6\sqrt{3}cA_1} \tag{5}$$

$$k_2=\frac{a^2}{\sqrt{3}c}\frac{4a^2+3c^2}{4a^2A_1+3c^2A_2}, \tag{6}$$

where A_1 and A_2 are defined by the equation

$$(l_{oi}-l_i)/l_{oi}=A_ip-B_ip^2; \quad i=1, 2$$

for the linear compressions perpendicular and parallel to the hexagonal axis. The force constants k_1 and k_2 apply respectively to bonds perpendicular and inclined to the hexagonal axis and a and c are the edges of the hexagonal unit cell. The corresponding equations for the white tin structure, $A5$, are

$$k_1=\frac{(4a^2+c^2)c}{4a^2A_1+c^2A_2} \tag{7}$$

$$k_2=(2a^2-c^2)/8cA_2. \tag{8}$$

The linear compressions perpendicular and parallel to the tetragonal axis are described by A_1 and A_2; a and c are the edges of the tetragonal unit cell, and k_1 and k_2 are the force constants for bonds inclined and parallel to the tetragonal axis.

It is found that the force constants (Table I) obtained in this way are linked with the interatomic distances by the relationship proposed by Badger[2] for force constants determined spectroscopically,

$$k^{-\frac{1}{3}}=a_{ij}(D_0-b_{ij}), \tag{9}$$

where a_{ij} and b_{ij} are constants and i, j indicate the rows in the periodic system in which the two partners are located. Only the case $i=j$ is treated here, since very few data for the general case are available (cf. below). The quantities a_{ii} and b_{ii} for the compressibility force constants differs somewhat from the corresponding terms for spectroscopic force constants, and the further restriction must be made that the long rows of the periodic system are to be subdivided into two parts. Table I contains the calculated force constants and the compressibilities and average interatomic distances used in the calculations. Figures 1 to 4 are graphical representations of the data. The straight lines correspond to the constants a_{ii} and b_{ii} given in Table II, together with the constants a'_{ii} and b'_{ii} used by Badger for spectroscopic force constants.

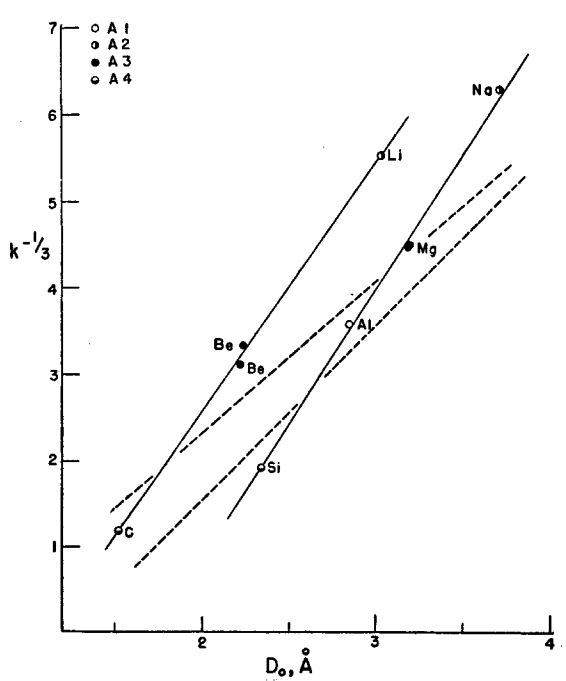

FIG. 1. Plot of the reciprocal of the cube root of the force constant of bonds *vs.* the interatomic distance for crystalline elements of the first and second short periods of the periodic system. The solid lines are curves of the Badger type drawn to represent the compressibility data, and the dashed lines are Badger's curves for the first-row and second-row elements, obtained from spectroscopic data for diatomic molecules.

TABLE II. Constants in relation 2
D_0 in A, k in megadynes/cm.

Elements	a_{ij}	b_{ij}	a'_{ij}[a]	b'_{ij}[a]
C, Be, Li	2.89	1.13	1.75	0.68
Na, Mg, Al, Si	3.10	1.73	2.04	1.25
(K), Ca, Ti, V, Ge	2.06	1.46	1.98	1.48
Cr, Fe, Co, Ni, Cu	13.3	2.31		
(Rb), Sr, Zr, Cb, Mo, Sn	2.32	1.86	2.04	1.76
Ru, Rh, Pd, Ag	4.12	2.10		
Ba, Ta, W	2.03	1.80		
Ce, Ir, Pt, Au, Tl	2.96	1.99		

[a] Corresponding constants used by Badger (see reference 2) for spectroscopic force constants.

DISCUSSION

It is interesting that for several elements in each period a relation of the Badger form holds quite well, and, moreover, that the Badger equations themselves (dashed lines in Figs. 1 to 3), which were derived completely from spectroscopic data for diatomic molecules, fit the compressibilities moderately well for some elements of the two long periods.

We might expect in general that the simple Badger relation would hold for crystals (or molecules) in which

the bond type (electronic structure) remains constant during compression. If, however, the electronic structure were to undergo a readjustment on compression, decreasing the energy of the system, the potential energy curve would be flattened, so that the force constant would be smaller and the compressibility greater than for the normal case in which this change in electronic structure does not occur. This phenomenon would cause the points in the plots of $k^{-\frac{1}{3}}$ against D_0 to lie above the normal Badger-rule lines for those substances showing such readjustment in electronic structure. We think that most of the features shown in Figs. 1 to 4 can be explained in this way.

It is reasonable to assign to the elements diamond, silicon, germanium, and grey tin, with the diamond

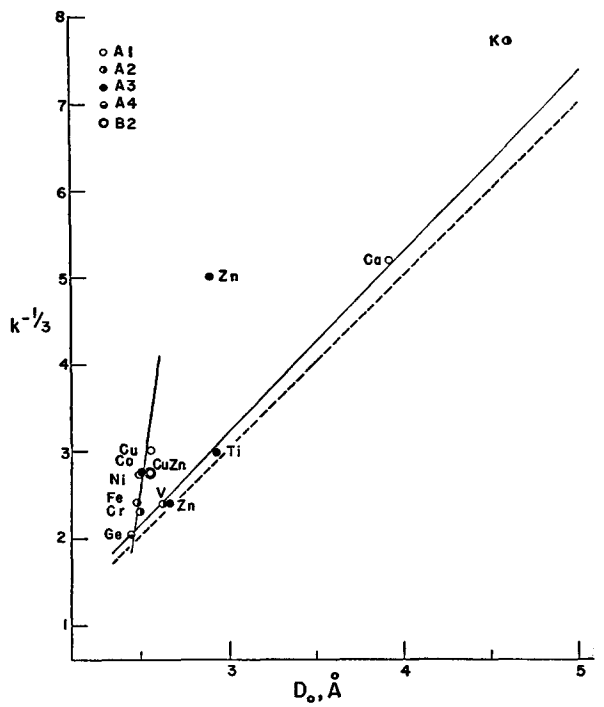

FIG. 2. Diagram showing the reciprocal of the cube root of the force constant for bonds of elements of the first long period, as a function of interatomic distance. The dashed line is Badger's spectroscopic curve.

arrangement, an electronic structure in which each atom is attached to each of its four ligates by an sp^3 single bond, and to expect this electronic structure to remain unchanged in nature on compression. The compressibilities of these elements should, then, correspond to their respective normal Badger-rule lines. Good agreement with the spectroscopic lines is indeed shown by germanium and grey tin, but the points for carbon and silicon are below their lines. Possibly the spectroscopic Badger lines for the first and second periods lie above the "normal" lines (corresponding to constant electronic structure) because of a change of electronic structure with changing interatomic distance for the diatomic molecules that provide the spectro-

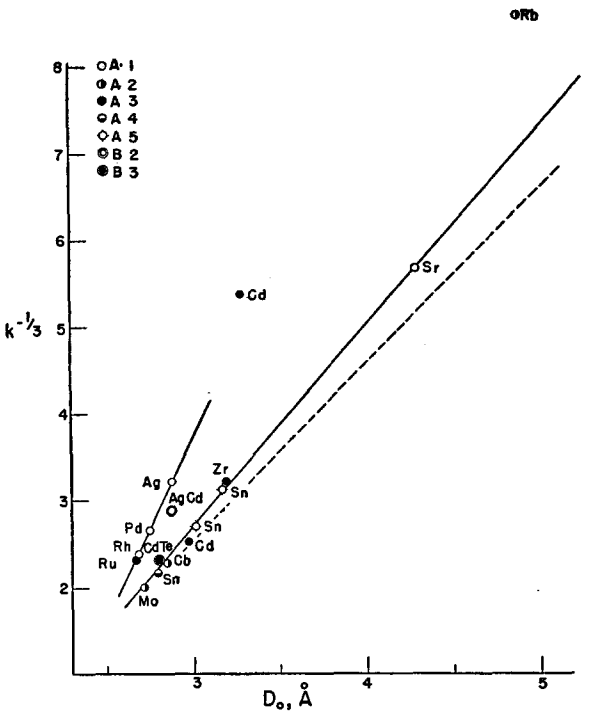

FIG. 3. Diagram showing the reciprocal of the cube root of the force constant for bonds of elements of the second long period, as a function of interatomic distance. The dashed line is Badger's spectroscopic curve.

scopic data. For most of these molecules the bond orbitals are not those corresponding to sp^3 hybridization, but are hybrids of a different nature (with more s character if the atoms have no σ unshared electron pairs, as in Li_2, and more p character if they have these unshared pairs, as in N_2), and on decrease of the interatomic distance the hybridization would be expected to change (toward sp^3 bond orbitals), leading to smaller force constants than normal.

The normal Badger lines for the two short periods may from this argument be expected to lie just below the spectroscopic lines of Fig. 1, being parallel to them and passing through the points for diamond and silicon. The high values of the other elements are presumably due to a similar change in hybridization of the bond orbitals. For one, two, and three valence electrons, the bond orbitals would have an amount of p character lying between the values minimizing the atomic energy, 0, 50 percent, and $66\frac{2}{3}$ percent, respectively (resulting from utilization of all of the s orbital), and the value giving the strongest bonds, presumably 75 percent, for sp^3 bond orbitals. At zero pressure the amount of p character seems to lie about midway between these extremes: the values 41 percent for lithium and 27 percent for sodium have been estimated by a simple calculation.[6] On compression the amount of p character would increase, and this change in bond type would lead to larger compressibilities than normal. The effect

[6] L. Pauling, Proc. Roy. Soc. (London) **196A**, 343 (1949).

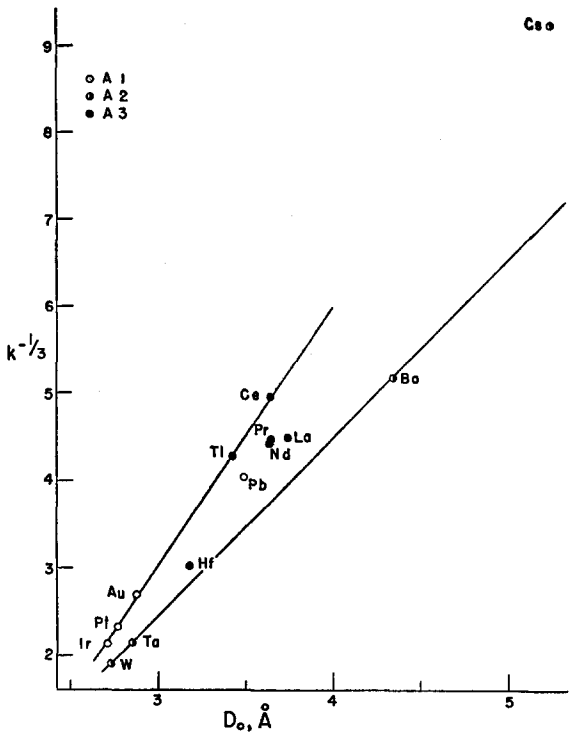

FIG. 4. Diagram showing the reciprocal of the cube root of the force constant for bonds of elements of the very long period, as a function of interatomic distance.

would be small for boron and aluminum, which have only the range of p character from $66\frac{2}{3}$ percent to 75 percent available, larger for beryllium and magnesium, and still larger for lithium and sodium; hence in a qualitative way it corresponds to a rotation of the lines around the points for diamond and silicon. Possibly a quantitative discussion of the effect would provide an explanation of the fact that the experimental points continue to approximate closely to straight lines.

For the first long period (Fig. 2) the points for calcium, titanium, vanadium, and germanium determine a straight line that lies only slightly above Badger's spectroscopic line, and the point for potassium lies considerably above the line. Similarly a straight line representing only a small rotation from Badger's line is determined for the second long period (Fig. 3) by the points for strontium, zirconium, columbium, molybdenum, and tin, the point for rubidium lying high. These facts suggest that the hybridization effect is less for these long periods than for the short periods, and that it is large only for the alkali metals.

Aside from germanium and tin, which have been discussed above, the elements fitting these lines (calcium to vanadium and strontium to molybdenum) are those that use all of their electrons outside of their noble-gas shell as metallic bonding electrons, and thus have fixed electronic structures, except for change in hybridization. (The point for chromium, which should be included in this group, lies slightly above the line.) The other metals of these long periods have more complex electronic structures, involving both metallic bonding electrons and atomic electrons outside of a noble-gas shell; and for each of these metals the electronic state is described in terms of resonance between two or more structures.[6] For iron, cobalt, and nickel the structures differ in the number of unpaired atomic electrons, and for copper and zinc (and also iron) in the number of bonding electrons. We attribute the large values of the compressibility of these elements to a change in the contributions of these resonating structures on compression; without, however, having a sufficient understanding of the phenomenon to account for the fact that the points seem to determine straight lines with slopes much greater than normal.

The points for the very long period (Fig. 4) can be enclosed by two straight lines. The lower one, which presumably lies only slightly above the normal Badger line (a spectroscopic line has not been determined), passes through the points for barium, tantalum, and wolfram. The point for cesium lies much above it, and those for lanthanum and hafnium, which would be expected to lie on it, are slightly high. The upper line is nicely determined by iridium, platinum, gold, thallium, and cerium, all of which have been assigned resonating structures (between the valences 2 and 3 for thallium, and 3 and 4 for cerium). It is interesting that the deviation for praseodymium and neodymium is just half as great as for cerium, and that the contribution of the quadrivalent structures for these elements (valence 3.1) has also been estimated[7] from their magnetic properties to be just half that for cerium (valence 3.2).

The evidence from the values of the interatomic distance and the magnetic susceptibility that ordinary metallic cerium has valence 3.2, together with the stability of quadrivalent cerium in many compounds, led us to predict that a very dense form of the metal, representing the metallic valence 4, could be made. At our suggestion Professor J. H. Sturdivant and Dr. Adam Schuch began the search for a method of preparing this form of cerium, which was finally successful.[8] The fact that the compressibility of cerium increases with increasing pressure, reaching double its initial value at 2830 kg/cm², whereas the compressibility of most metals decreases with increasing pressure, indicates that the valence of cerium increases rapidly under compression. Transition to the quadrivalent state has been found to have taken place at 15,000 kg/cm².[9]

The compressibility of lead indicates a small resonance effect for this metal, and thus supports the suggestion[6] that the structure of the metal is almost entirely determined by the bivalent state of the atom.

Zinc and cadmium crystallize in a deformed $A3$ arrangement, with axial ratio such that each atom has

[7] L. Pauling, J. Am. Chem. Soc. **69**, 542 (1947).
[8] A. Schuch and J. H. Sturdivant, J. Chem. Phys. **18**, 145 (1950).
[9] A. W. Lawson and T.-Y. Tang, Phys. Rev. **76**, 301 (1949).

six ligates at a small distance and six at a larger distance. For each element the small distance corresponds to half-bonds, and the larger distance to weaker bonds, with bond number about $\frac{1}{6}$. It has been suggested[6] that the deformation from the normal axial ratio 1.633 for the $A3$ arrangement, which would surround each atom with twelve equidistant ligates, is the result of the special stability of six half-bonds, corresponding to resonance of three bonds for each atom among six positions, and that the remaining valences of the atom are divided among the other six positions. The normal valence of zinc and cadmium is $4\frac{1}{2}$, corresponding to resonance in the ratio 3:1 between the quadrivalent state (with a metallic orbital) and the sexivalent state. The longer bond distances suggest, however, a smaller valence, about 4, at zero pressure. The observed compressibilities provide further information about the structure of these elements. For each of them the force constant for the shorter bonds is normal, whereas that for the longer bonds indicates that a change in bond type occurs on compression (Figs. 2 and 3). We may hence conclude that even when strained the shorter bonds remain half-bonds, with no change in the basal-plane electronic structure, but that the longer bonds undergo an increase in bond number when the crystal is compressed along the c axis, with increase in the valence of the metal.

White tin has a tetragonal structure somewhat resembling the hexagonal structures of zinc and cadmium; each tin atom forms four strong bonds, lying nearly in the basal plane, and two weaker ones, parallel to the c axis. The distances indicate bond numbers $\frac{1}{2}$ and $\frac{1}{4}$, respectively, corresponding to the normal metallic valence $2\frac{1}{2}$ (3:1 resonance between bivalent and quadrivalent tin). The behavior on compression is, however, different from that of zinc and cadmium; the point for the longer bonds of tin in Fig. 3, like that for the shorter bonds, lies on the lower curve, indicating that no change in bond type occurs on deformation of the crystal. We attribute the difference in behavior of tin from that of zinc and cadmium to the fact that tin has its normal metallic valence at normal pressure, and so does not tend to undergo a change in valence under compression.

Indium seems to represent a transition between cadmium and white tin. Indium has the $A6$ structure, a tetragonal variant from cubic closest packing. Only the volume compressibility has been determined. Each atom has four ligates at 3.242A and eight at 3.370A. If the $A1$ formula is used, with 3.327A as the average distance, k is calculated from the compressibility to be $1.38 \cdot 10^{-2}$, and $k^{-\frac{1}{3}}$ to be 4.17. This value is intermediate between those, 3.46 and 5.08, corresponding to the lower and upper lines of Fig. 3.

Force constants were also calculated for a number of compounds of simple structure (including alloys) involving one kind of nearest-neighbor bonds only. Table I contains these data for compounds with bonds of at least 50 percent covalent character as evidenced by the electronegativities of the constituents.[10] No general fit was obtained with Eq. (9), however, and unfortunately not enough data are available to show any general trend. Moreover since a large fraction of these compressibilities were measured with slugs of compressed powder, the reliability of part of the data is questionable. For example, the compressibility of a sample of powdered magnesium oxide was found[11] to be almost twice as great as that of the single crystal. The initial compression of finely powdered lead[12] is about 50 percent higher than that of the solid metal even after exposure to a pressure of 25,000 kg/cm^2, and only at higher pressures is the compression of the sample sensibly the same as that of the cast metal. The compressibilities of the alloys in Table I were determined from cast samples and should therefore be reliable. Bridgman made the observation that alloys showed much more irregularity and more hysteresis under compression that did the elements. Only for three alloys of simple structure with components from the same row of the periodic system (CuZn, AgCd, and CdTe) are the compressibilities available. The corresponding force constants are plotted in the appropriate figures. It is seen that Eq. (9) holds reasonably well for them.

With increasing pressure the compressibilities generally decrease, the force constants increasing with decreasing interatomic distance, as is shown by the negative values of the constants k' collected in Table I. The exception of cerium is attributed to increase in metallic valence on compression, as discussed above. The values of k' seem not to depend in any simple manner on position in the periodic table.

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[11] P. W. Bridgman, Proc. Am. Acad. **67**, 345 (1932).
[12] P. W. Bridgman, Proc. Am. Acad. **76**, 9 (1945).